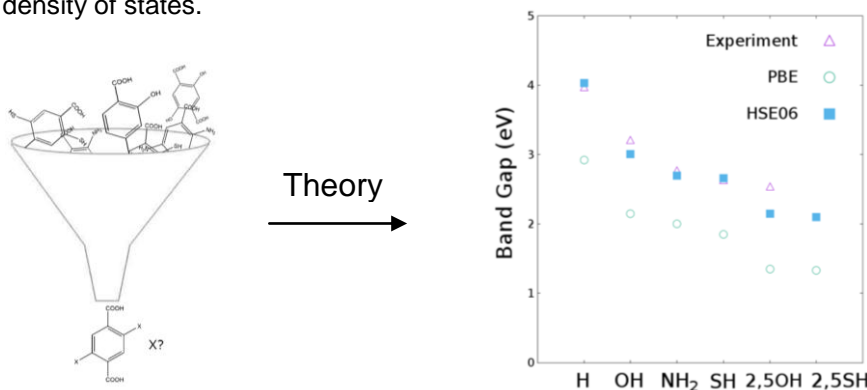


## Engineering light-absorption in MOFs: Combined experimental and theoretical study of UiO-66

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The importance of renewable energy sources has become apparent with the increasing environmental concerns, and much research focuses on the use of sunlight for photochemical, catalytic transformations. To produce a useful photocatalyst, the system has to efficiently harvest (solar) energy and combine high activity with recyclability and stability. Hybrid materials, e.g. Metal-Organic Frameworks (MOFs) have already shown interesting potential for photo-catalytic applications. The large band gap of most MOFs normally limits their use to the UV region of the spectrum. However, (post-)functionalizing the organic linkers allows to shift this absorption towards the visible region.<sup>1,2</sup> This contribution focusses on the stable UiO-66 framework, built out of Zr-O nodes and (functionalized) terephthalic acid linkers. The NH<sub>2</sub>-functionalized version has a known visible light absorption shift<sup>3</sup> and has been investigated well together with the -NO<sub>2</sub> functional group. We extend this research to other functional groups (UiO-66-X with X=H, OH, (OH)<sub>2</sub>, NH<sub>2</sub>, SH) and rationalize the processes via ab initio calculations. Combination of experimental measurements and theoretical calculations allows to gain deeper insight into the electronic structure of the frameworks. We performed TD-DFT calculations on the isolated linkers to rationalize the changing absorption properties and on cluster models. The linker calculations are compared to ground state DFT calculations of the full periodic material (figure 1), allowing to better understand the influence of the framework environment on the absorption properties of the MOF. Study of the periodic material revealed insight in the nature of the electronic changes via in-depth analysis of the density of states.



**KEYWORDS:** UiO-66, metal-organic framework, TDDFT, photocatalysis

<sup>1</sup> C.H. Hendon, D. Tiana, M. Fontecave, C. Sanchez, L. D'arras, C. Sassoye, L. Rozes, C. Mellot-Draznieks and A. Walsh, *J. Am.Chem.Soc.*, 135 (2013) 10942.

<sup>2</sup> M.A. Nasalevich, M. van der Veen and J. Gascon, *CrystEngComm.*, 16 (2014) 4919

<sup>3</sup> S. Dengrong, F. Yanghe, L. Wenjun, Y. Lin, W. Dengke, Y. Lin, F. Xianzhi and L. Zhaohui, *Chem. Eur. J.*, 19 (2013) 14279